Collisional excitation of interstellar sulfur dioxide

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ABSTRACT

Rotational excitation rates for sulfur dioxide in collisions with He atoms at temperatures from 25 - 125 K, obtained from theoretical calculations by Palma (1987), have been reanalyzed in terms of corrected asymmetric top rotational wavefunctions.

In a paper with the same title, Palma (1987) presented theoretical values for rates of rotational excitation of sulfur dioxide, SO_2, in collisions with He atoms. These rates are needed to analyze observations of this molecule in the interstellar gas. Unfortunately, the asymmetric top rotational levels between which Palma (1987) reported collision rates do not correspond with the subset of rotational levels which are allowed by nuclear spin statistics for the identical oxygen nuclei. The present work reanalyzes the earlier work to obtain collision rates among the appropriate rotational levels. It appears, as discussed below, that the only error in the earlier study was the final step, which involves combining the asymmetric top rotor wavefunctions with the "generalized infinite order sudden (IOS)" rates to obtain state-to-state rates among the asymmetric top levels. Therefore, the earlier work will be reviewed only briefly.

The interaction potential between SO_2 and a He atom was obtained within an approximate electron gas formalism (Gordon & Kim 1972). This method provides a reasonable approximation to more exact quantum methods with a fraction of the computational expense. In particular, it gives a reasonable estimate for the shape of the short-range potential which dominates rotational excitation in this system at collision energies of more than about 50 K. The molecular scattering calculations used the IOS approximation in which state-to-state rates are obtained from "generalized IOS rates", $Q(L,M_1,M_2)$. These are obtained from an expansion of the angle dependence of the collisional S-matrices in terms of spherical harmonics. Calculations were done with an early version of the MOLSCAT computer code (Hutson & Green 1994). In 1986 a program error was inadvertently introduced into the routine which computes associated Legendre polynomials in MOLSCAT, version 9, and which is used to evaluate the spherical harmonics, and this was not discovered and corrected until 1993 in MOLSCAT, version 11. Fortunately, the calculations in Palma (1987) were performed before this error occurred. The other programs used for obtaining the interaction potential and obtaining a fit to this potential in terms of spherical harmonics have been used routinely

in this laboratory for many years and are believed to be correct. It is therefore believed that the generalized IOS rates presented in Table 2 of Palma (1987) are correct.

The asymmetric top rotor wavefunctions, on the other hand, do not correspond to the allowed rotational levels in this system. It is important for the scattering calculation to expand these wavefunctions in terms of symmetric top wavefunctions evaluated in the same coordinate system used to describe the interaction potential; the resulting moments of inertia, I_x, I_y, and I_z are not necessarily in the ascending order conventionally used by spectroscopists (see, e.g., Green 1976). Using the molecular geometry for SO_2 reported by Palma (1987) the rotation constants about the x, y, and z axes are calculated to be 0.295, 1.99, and 0.347 cm^{-1}, respectively, which can be compared with the values 0.293535, 2.02736, and 0.34417 cm^{-1} tabulated by Herzberg (1966). The symmetry axis (z-axis) corresponds, in standard spectroscopic notation, to the b-axis, for which case nuclear spin statistics for the identical oxygen nuclei allow only $J(K_{-1},K_1)$ asymmetric top levels with (K_{-1},K_1) either *ee* or *oo*, where *e/o* indicates even/odd integer values. Asymmetric top wavefunctions for this case are also restricted to expansions in symmetric top functions with even k, where k is the projection of the rotational momentum on the symmetry axis, as noted correctly by Palma (1987). It is possible that Palma (1987) mistakenly adopted symmetry restrictions from the very similar SiC_2 molecule for which Palma & Green (1987) had previously presented collision rates. For SiC_2, however, the symmetry axis is along the spectroscopic a-axis, in which case the restrictions on allowed wavefunctions are K_{-1} even and k even.

Using the rotation constants from Herzberg (1966), asymmetric top functions expanded in symmetric top wavefunctions in the axis system corresponding to the collision coordinates were computed by diagonalizing the rigid rotor Hamiltonian. The asymmetric top wavefunctions are written explicitly as

$$|J;K_{-1},K_1;m\rangle = \sum_{k\geq 0} a_k \ (1+\delta_{k,0})^{-1} \ (\ |J,k,m\rangle \ + \ \varepsilon_{J;K_{-1},K_1} \ |J,-k,m\rangle \ ) \ ,$$

where J is the is the total rotor angular momentum, m its projection on a space-fixed axis, k its projection on the (principal moment of inertia) molecule-fixed axis, $\delta_{i,j}$ is a Kronecker delta function equal to one for i=j and to zero otherwise, and $|J,k,m\rangle$ are symmetric top wavefunctions. Values of a_k and ε required to specify each of the lowest 50 rotational levels are reported in Table 1.

Using these rotational wavefunctions and the $Q(L,M_1,M_2)$ reported by Palma (1987) collision rates were recomputed. Because the IOS approximation ignores rotational energy spacings compared with the collision energy, IOS rates for downward transitions are not related by detailed balance to rates for corresponding upward transitions as is required for the correct values. It is currently believed that the IOS approximation is more accurate for computing the downward rates (DePristo et al. 1979) and only these are reported; the upward rates can be calculated from detailed balance. Rates between the lowest 10 levels are reported in Table 2, ordered by energy of the initial level, and, for each initial level, on the energy of the final level, for final levels of lower energy than the initial level. Values between all 50 levels may be obtained from the author.[1]

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[1] Files of the energy levels and rate constants are available via anonymous ftp from molscat.giss.nasa.gov in directory pub/astrophysics. The file names are so2_levels and so2_rates, respectively. These and other collision rate constants may also be obtained via the World Wide Web by connecting to URL "http://molscat.giss.nasa.gov/rates/". S. Green may be reached by electronic mail at agxsg@nasagiss.giss.nasa.gov.

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For a transition between levels with rotational quantum numbers j_1 and j_2, $Q(L,M_1,M_2)$ are required with $L \leq j_1+j_2$ and $M_1,M_2 \leq L$. Not all of the required $Q(L,M_1,M_2)$

were available from Palma (1987) for some of the higher levels, but contributions from the missing values with high indices are generally small and are not expected to affect reported rates significantly. The discussion of expected accuracy of the resulting collision rates which was given by Palma (1987) is believed to be correct and applies to the present values as well.

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Table 1. SO_2 rotational eigenvalues and eigenfunctions

	$J(K_{-1}, K_1)$	Energy[a]	ε	a_0	a_2	a_4	a_6	a_8	a_{10}	a_{12}
1	0(0, 0)	0.000	+	1.00000						
2	2(0, 2)	1.912	+	-0.51107	-0.60779					
3	1(1, 1)	2.321	+	1.00000						
4	2(1, 1)	3.698	-	0.00000	-0.70711					
5	3(1, 3)	5.382	+	-0.61797	-0.55593					
6	4(0, 4)	6.360	+	-0.40240	-0.41220	-0.49913				
7	4(1, 3)	8.336	-	0.00000	-0.25988	-0.65762				
8	2(2, 0)	8.748	+	-0.85954	0.36138					
9	3(2, 2)	10.660	-	0.00000	0.70711					
10	5(1, 5)	10.887	+	-0.49626	-0.47259	-0.39182				
11	4(2, 2)	13.227	+	-0.54458	-0.33048	0.49244				
12	6(0, 6)	13.314	+	0.35940	0.35831	0.36068	0.42064			
13	6(1, 5)	15.614	-	0.00000	0.15435	0.32353	0.60951			
14	5(2, 4)	16.396	-	0.00000	-0.36138	-0.60779				
15	7(1, 7)	18.825	+	0.43283	0.41910	0.37677	0.29787			
16	3(3, 1)	19.203	+	-0.78620	0.43697					
17	6(2, 4)	20.295	+	-0.42730	-0.34204	-0.07164	0.53533			
18	4(3, 1)	21.757	-	0.00000	-0.65762	0.25988				
19	8(0, 8)	22.728	+	-0.34089	-0.33690	-0.32635	-0.31584	-0.34948		
20	7(2, 6)	24.673	-	0.00000	0.23298	0.42454	0.51525			
21	5(3, 3)	24.949	+	0.51582	0.20252	-0.57092				

#	State	Energy		1	2	3	4	5	6	7
22	8(1, 7)	25.520	-	0.00000	0.11078	0.22244	0.34466	0.36521		
23	6(3, 3)	28.782	-	0.00000	0.39910	0.46766	-0.34930			
24	9(1, 9)	29.186	+	0.39394	0.38426	0.35530	0.30669	0.23337		
25	8(2, 6)	29.990	+	0.35312	0.30732	0.16831	-0.07729	-0.55579		
26	7(3, 5)	33.253	+	0.41902	0.27891	-0.10074	-0.56945			
27	4(4, 0)	33.714	+	0.73587	-0.46998	0.09149				
28	10(0,10)	34.552	+	0.33282	0.32792	0.31384	0.29279	0.27074	0.28207	
29	9(2, 8)	35.480	-	0.00000	0.16965	0.31766	0.42023	0.44014		
30	5(4, 2)	36.905	-	0.00000	-0.60779	0.36138				
31	10(1, 9)	38.029	-	0.00000	-0.08885	-0.17534	-0.25926	-0.34902	-0.52185	
32	8(3, 5)	38.373	-	0.00000	-0.27326	-0.41989	-0.29781	0.40041		
33	6(4, 2)	40.735	+	0.49099	0.11059	-0.57558	0.18958			
34	11(1,11)	41.956	+	-0.36794	-0.36036	-0.33794	-0.30144	-0.25141	-0.18485	
35	10(2, 8)	42.350	+	0.29770	0.26875	0.18240	0.03850	-0.17345	-0.56447	
36	9(3, 7)	44.121	+	0.36117	0.28238	0.06209	-0.24823	-0.53811		
37	7(4, 4)	45.205	-	0.00000	0.41397	0.33628	-0.46426			
38	12(0,12)	48.742	+	0.32841	0.32332	0.30848	0.28519	0.25590	0.22571	0.22049
39	11(2,10)	48.805	-	0.00000	-0.13336	-0.25299	-0.34521	-0.39516	-0.37801	
40	8(4, 4)	50.314	+	-0.40415	-0.21827	0.21610	0.50917	-0.25444		
41	10(3, 7)	50.544	-	0.00000	0.20253	0.34175	0.35412	0.16481	-0.43547	
42	5(5, 1)	52.279	+	0.69832	-0.48544	0.14327				
43	12(1,11)	53.114	-	0.00000	-0.07682	-0.15032	-0.21802	-0.27987	-0.34357	-0.47708
44	9(4, 6)	56.064	-	0.00000	0.29995	0.38565	0.11020	-0.49916		
45	6(5, 1)	56.108	-	0.00000	-0.56293	0.42026	-0.08053			
46	13(1,13)	57.122	+	-0.34951	-0.34321	-0.32464	-0.29473	-0.25482	-0.20600	-0.14664
47	12(2,10)	57.403	+	0.25425	0.23392	0.17383	0.07609	-0.05818	-0.23779	-0.56305

48 11(3, 9) 57.556 + -0.32049 -0.26987 -0.12620 0.08557 0.32120 0.49939
49 7(5, 3) 60.576 + 0.47089 0.04355 -0.54962 0.29181
50 10(4, 6) 62.456 + -0.35228 -0.24305 0.03637 0.34072 0.41357 -0.30070

a. Energy in cm^{-1}.

Table 2.   State-to-state collision rates[a]

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$J(K_{-1}, K_1)$		Temperature, kelvin				
initial	final	25.0	50.0	75.0	100.0	125.0
2(0, 2) -	0(0, 0)	8.37D-12	1.08D-11	1.17D-11	1.23D-11	1.26D-11
1(1, 1) -	0(0, 0)	2.86D-12	4.97D-12	6.37D-12	7.33D-12	8.07D-12
1(1, 1) -	2(0, 2)	4.26D-12	6.09D-12	7.15D-12	7.87D-12	8.44D-12
2(1, 1) -	0(0, 0)	0.00D+00	0.00D+00	0.00D+00	0.00D+00	0.00D+00
2(1, 1) -	2(0, 2)	5.62D-12	9.10D-12	1.13D-11	1.29D-11	1.41D-11
2(1, 1) -	1(1, 1)	1.59D-11	2.03D-11	2.22D-11	2.34D-11	2.42D-11
3(1, 3) -	0(0, 0)	1.37D-12	1.73D-12	1.89D-12	2.00D-12	2.09D-12
3(1, 3) -	2(0, 2)	5.21D-12	8.80D-12	1.10D-11	1.25D-11	1.36D-11
3(1, 3) -	1(1, 1)	6.67D-12	8.91D-12	9.82D-12	1.03D-11	1.07D-11
3(1, 3) -	2(1, 1)	6.21D-12	9.45D-12	1.11D-11	1.20D-11	1.27D-11
4(0, 4) -	0(0, 0)	1.03D-12	1.86D-12	2.30D-12	2.59D-12	2.78D-12
4(0, 4) -	2(0, 2)	1.35D-11	1.87D-11	2.10D-11	2.25D-11	2.35D-11
4(0, 4) -	1(1, 1)	1.61D-12	2.53D-12	3.06D-12	3.40D-12	3.63D-12
4(0, 4) -	2(1, 1)	2.94D-12	4.29D-12	5.03D-12	5.51D-12	5.85D-12
4(0, 4) -	3(1, 3)	2.57D-12	4.95D-12	6.64D-12	7.84D-12	8.72D-12
4(1, 3) -	0(0, 0)	0.00D+00	0.00D+00	0.00D+00	0.00D+00	0.00D+00
4(1, 3) -	2(0, 2)	8.41D-13	1.23D-12	1.44D-12	1.58D-12	1.67D-12
4(1, 3) -	1(1, 1)	2.78D-12	4.89D-12	5.98D-12	6.64D-12	7.05D-12
4(1, 3) -	2(1, 1)	1.17D-11	1.56D-11	1.75D-11	1.87D-11	1.95D-11
4(1, 3) -	3(1, 3)	7.75D-12	1.13D-11	1.33D-11	1.47D-11	1.56D-11
4(1, 3) -	4(0, 4)	6.66D-12	1.11D-11	1.39D-11	1.59D-11	1.73D-11
2(2, 0) -	0(0, 0)	1.17D-12	2.02D-12	2.68D-12	3.17D-12	3.55D-12
2(2, 0) -	2(0, 2)	1.79D-12	3.17D-12	4.18D-12	4.91D-12	5.47D-12

2(2, 0) - 1(1, 1)	3.12D-12	5.43D-12	7.09D-12	8.33D-12	9.31D-12
2(2, 0) - 2(1, 1)	2.27D-12	3.99D-12	5.23D-12	6.13D-12	6.85D-12
2(2, 0) - 3(1, 3)	2.92D-12	3.95D-12	4.56D-12	5.02D-12	5.40D-12
2(2, 0) - 4(0, 4)	8.27D-13	1.40D-12	1.72D-12	1.93D-12	2.07D-12
2(2, 0) - 4(1, 3)	2.67D-12	4.02D-12	4.80D-12	5.31D-12	5.68D-12
3(2, 2) - 0(0, 0)	0.00D+00	0.00D+00	0.00D+00	0.00D+00	0.00D+00
3(2, 2) - 2(0, 2)	2.51D-12	4.29D-12	5.57D-12	6.51D-12	7.22D-12
3(2, 2) - 1(1, 1)	6.94D-13	1.03D-12	1.25D-12	1.42D-12	1.56D-12
3(2, 2) - 2(1, 1)	3.86D-12	6.09D-12	7.59D-12	8.69D-12	9.56D-12
3(2, 2) - 3(1, 3)	2.78D-12	5.18D-12	6.86D-12	8.05D-12	8.96D-12
3(2, 2) - 4(0, 4)	1.25D-12	2.36D-12	3.13D-12	3.69D-12	4.11D-12
3(2, 2) - 4(1, 3)	2.23D-12	4.06D-12	5.31D-12	6.18D-12	6.83D-12
3(2, 2) - 2(2, 0)	1.56D-11	2.06D-11	2.26D-11	2.38D-11	2.45D-11
5(1, 5) - 0(0, 0)	8.12D-13	1.51D-12	1.93D-12	2.20D-12	2.37D-12
5(1, 5) - 2(0, 2)	3.18D-12	5.11D-12	6.36D-12	7.22D-12	7.85D-12
5(1, 5) - 1(1, 1)	6.01D-13	1.10D-12	1.40D-12	1.62D-12	1.79D-12
5(1, 5) - 2(1, 1)	4.87D-13	1.01D-12	1.40D-12	1.70D-12	1.94D-12
5(1, 5) - 3(1, 3)	1.14D-11	1.57D-11	1.74D-11	1.85D-11	1.91D-11
5(1, 5) - 4(0, 4)	3.77D-12	6.87D-12	9.15D-12	1.08D-11	1.21D-11
5(1, 5) - 4(1, 3)	2.55D-12	4.43D-12	5.58D-12	6.36D-12	6.92D-12
5(1, 5) - 2(2, 0)	8.96D-13	1.66D-12	2.13D-12	2.44D-12	2.65D-12
5(1, 5) - 3(2, 2)	1.37D-12	1.89D-12	2.22D-12	2.48D-12	2.69D-12

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a. The notation 1.23D-11 indicates 1.23×10^{-11}; units are $cm^3 s^{-1}$.